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PHOTOEXCITATIONS IN PERNIGRANILINE: RING-TORSIONAL POLARONS AND BOND-ORDER SOLITONS

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ABSTRACT

We report the first near-steady-state and long-time photoinduced-absorption spectroscopies of pernigraniline base, a novel Peierls ground state polymer with multiple order parameters. Two kinds of defects have been observed and distinguished by differing time domains and ir active vibrations. The short-lived defect has a lifetime of msec scale and a defect mass of $\sim 5 m_e$; in contrast, the lifetime of the long-lived defect (mass $\sim 300 m_e$) is greater than several hours at low temperatures. We propose that the short-lived excitation is a soliton defect in the bond length [order parameter or alternation], while the long-lived excitation is a polaron defect in the ring torsion angle order parameter.

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Soliton and polaron defects in the bond length alternation of conjugated polymers such as polyacetylene and polythiophene have been extensively studied.¹ Similar excitations have been predicted to be stable in the pernigraniline base (PNB) form of polyaniline, which is suggested to have a Peierls band gap with a two-fold degenerate ground state,² the first such system beyond polyacetylene. However, in contrast to polyacetylene, there is an additional order parameter to be considered, the periodicity in the phenyl ring torsion angle, giving rise to the possibility of ring-torsional polaronic and solitonic defects.³ Recently, calculations have predicted that the two order parameters will act independently, additively contributing to the Peierls gap.⁴ The successful synthesis of PNB^{5,6} has created the opportunity to test the presence of multiple order parameters and their roles in the Peierls ground state and its excitations.⁷

We report here the first photoinduced-absorption spectra of pernigraniline. Two types of defect states are observed, namely long-lived and short-lived defects. The long-lived defect is associated with a 1.5-eV photoinduced-absorption peak, a set of long-lived photoinduced infrared active vibrational (IRAV) modes, and is massive ($\sim 300 m_e$). This long-lived massive defect can be understood in the picture of ring-torsional dimerization proposed by Ginder and Epstein³. In addition to the long-lived defects, short-lived photoinduced IRAV modes associated with short-lived photoinduced-absorption peaks at 1.0 and 1.3 eV are detected. The estimated defect mass from this photoinduced-absorption spectrum is comparatively small ($\sim 5 m_e$), in agreement with the calculations by dos Santos and Brédas of the bond length changes of these solitons.² These experimental results demonstrate that PNB indeed has a Peierls gap with multiple independent order parameters including bond-order u and ring-angle torsion Ψ . The long-lived massive photoinduced absorption originates from the massive ring-rotational polaron while the short-lived defect is the low mass bond length soliton.

The chemical structure of PNB is shown in Figure 1 with (a) undimerized and (b) dimerized structures. For the undimerized PNB structure, there is one unpaired electron

per each repeat unit (N-ring) of projected length a along the chain axis, forming a half-filled metallic energy band. However, as described by the Peierls theorem, the lattice is subject to a spontaneous symmetry-breaking, i.e. a Peierls gap forms at $k_F = \pi/2a$, and the polymer becomes an insulator. In a way similar to *trans*-polyacetylene, a bond length order wave (BOW) forms in PNB. Here, the shorter bond is a quinoid structure with C=N double bond, while the longer bond is a benzenoid structure with C-N single bond, Figure 1(b). Dos Santos and Brédas² studied the ground state and the nonlinear excitations in PNB. From their results, the defect mass of the BOW soliton is estimated to be $\sim 5 m_e$.

One noticeable difference between pernigraniline base and *trans*-polyacetylene¹ is that the former contains rings while the latter does not. In dos Santos and Brédas' treatment, the rings are renormalized and suppressed into effective bonds. While this simplification makes it possible to describe pernigraniline base in the Su-Schrieffer-Heeger (SSH) model,⁸ the ring-angle rotation effect is not explicitly described by this simplified model. Recently, the central role of ring-torsion-angle freedom in ring-containing polymers was proposed³. In addition to the electron-phonon interaction, it is expected that there are couplings between nitrogen p_π orbitals and the ring π orbitals with a cosine dependence on the ring torsion angle Ψ . The ring torsion angle of the quinoid rings tends to be more planar than that of the benzenoid rings. Instead of alternating angles $\pm\Psi_0$ and $\mp\Psi_0$ as in leucoemeraldine base (LEB)³, PNB was proposed³ to have alternating torsion angles $\pm\Psi_0 \pm \delta$ and $\mp\Psi_0 \pm \delta$, where Ψ_0 is the average ring torsion angle, and δ is the deviation from the average ring angle. Typical values for both Ψ_0 and δ are $\sim 30^\circ$, based on quantum chemical calculations.⁴ It is anticipated that, due to the large moment of inertia of the rings, the ring-torsional defect is massive ($> 100 m_e$). Therefore, unlike *trans*-polyacetylene, the Peierls gap of pernigraniline base originates not only from bond-length dimerization (u), but also from ring-torsion-angle dimerization (δ).

The near-steady-state photoinduced-absorption experiments were carried out over a broad probe photon energy range (0.1–3.3 eV) using either a glow bar or tungsten lamp as

a probe source, filtered through a grating monochromator. The sample was photoexcited by the output of an argon-ion laser (2.4 eV). The pump beam was mechanically chopped at frequencies between 4 and 400 Hz. Defect lifetimes on the order of milliseconds can be detected by this apparatus. The long-time photoinduced-absorption experiment was carried out on a Nicolet 60SX Fourier Transform Infrared (FTIR) spectrometer (500–20,000 cm^{-1}). In this apparatus, lifetimes longer than a few seconds can be determined.

The near-steady-state photoinduced-absorption spectra of PNB in the range 0.5–3.3 eV at temperatures of 300 K and 10 K are shown in Figure 2. The spectrum at 300 K shows three photoinduced-absorption (PA) features, namely a low energy peak (LE) at 1.0, a middle energy peak (ME) at 1.5, and a high energy peak (HE) at 3.0 eV; and two photoinduced bleaching (PB) features, a broad PB (1.75–2.7 eV) and the onset of PB for energies greater than 3.3 eV. At a temperature of 10 K, the original LE peak is replaced by a peak at 1.0 eV (LE1) and a shoulder at 1.3 eV (LE2). We note that LE1 and LE2 are much stronger than LE, while HE is reduced in strength and shifted to 3.1 eV upon cooling. The crossover from photoinduced absorption to photoinduced bleaching occurs at ~ 1.63 eV at 300 K and ~ 1.71 eV at 10 K.

Figure 3 (left ordinate scale) shows the 10 K near-steady-state PA spectrum of PNB in a KBr pellet in the mid-infrared range (1000–12,000 cm^{-1} or 0.1–1.6 eV). PA peaks are found at 8,000 cm^{-1} (1.0 eV) and 12,000 cm^{-1} (1.5 eV). A shoulder is also seen at $\sim 10,000$ cm^{-1} (~ 1.3 eV). Photoinduced IRAV modes are found at 1100, 1220, 1320, 1580 cm^{-1} . Also shown in Fig. 3 (right ordinate scale) is the long-time PA spectrum of PNB in a KBr pellet at 80 K for the same mid-ir range, plotted by reducing its magnitude by a factor of ~ 400 . Only one peak was observed at 12,000 cm^{-1} (1.5 eV). Two major photoinduced IRAV modes are found at 1153, 1554 cm^{-1} and photoinduced bleaching peaks are found at 1219, 1323, 1487 and 1591 cm^{-1} .⁹

The data support that the origin of the 1.5-eV PA peak with corresponding IRAV modes is very different from that of the 1.0-eV PA peak and associated IRAV modes.

First, their defect masses are different. The defect mass can be estimated from the relative oscillator strengths of electronic transitions and IRAV modes utilizing the amplitude mode formalism.¹⁰ The ratio of electronic and IRAV oscillator strengths for the 1.5 eV defect is calculated to be ~ 3000 while this ratio is estimated to be ~ 80 for the 1.0 eV defect. Using a band effective mass of $0.14 m_e$ for PNB,⁹ the defect masses are estimated to be ~ 300 and $5-10 m_e$ for the 1.5-eV and the 1.0-eV defect, respectively. Second, the lifetimes of these two defects are very different. The 1.5-eV peak and associated IRAV (particularly 1153 cm^{-1} mode) are observed to have effective lifetimes of several hours or longer at 80 K. On the other hand the 1.0-eV broad peak which is observed in near-steady-state photoinduced absorption is completely absent in the long-time experiment. We conclude that the lifetime of the defect associated with the 1.0-eV PA peak is less than 20 s while the lifetime of that associated with the 1.5-eV PA peak is longer than 3 h at 80 K.

In order to measure (or estimate) the lifetime of the short-lived defect, the chopper frequency dependence was investigated in near-steady-state PA experiment. The 1.0 and 1.3 eV PA peaks have similar chopper frequency dependence with lifetimes estimated to be ~ 0.1 sec, which explains why the 1.0-eV defect is absent in long-time PA experiment. The PA of IRAV modes obey the same frequency dependence as the 1.0-eV peak, indicating that these IRAV modes are associated with 1.0-eV short-lived defect. To the lowest chopper frequency available in the near-steady-state photoinduced absorption experiment, the magnitude of ME and HE continue to increase, reflecting that the effective lifetimes of ME and HE are much longer than that of the LE features, consistent with the long-time experiment of pernigraniline.

Based on these experimental results, we propose that LE1 and LE2 originate from bond-length order soliton levels in PNB. We suggest that LE1 and LE2 correspond to optical transitions from the valence band to the empty type-II soliton level² and from filled type-I soliton level² to the conduction band, respectively. Optical transitions between the filled type-I soliton level to the empty type-II soliton level were not observed, which is

consistent with the fact that these two levels correspond to defects centered at different sites. Preliminary light-induced electron spin resonance (LESR) experiments suggest that the short-lived defects do not have spin. In contrast, a long-lived LESR signal is found to accompany the long-lived defect.¹¹

We tentatively propose that the IRAV modes of the short-lived photoinduced defects present at 1100, 1220, 1320, and 1580 cm^{-1} arise from symmetry breaking of the *para*-disubstituted benzene rings due to formation of bond length order solitons. Hence the formerly Raman active 1163, 1223, 1321, and 1594 cm^{-1} modes become ir active¹². An effective electron-phonon coupling parameter $2\bar{\lambda}$ is estimated to be ~ 0.8 and ~ 0.9 for the short-lived and long-lived defects in emeraldine base, respectively. A pinning parameter $\alpha \sim 0.8$ is found, larger than that of polyacetylene (~ 0.06)¹⁰ and polythiophene (~ 0.31).¹³

Two order parameters could be involved in the long-lived defects: δ and Ψ_0 . The model used here assumes that the three proposed order parameters are independent. Further work is necessary to understand the coupling between these order parameters.

We conclude that pernigraniline base is a novel Peierls ground state polymer with multiple order parameters u , δ , and Ψ_0 . Long-lived defects are observed in the long-time PA experiment with large defect mass ($\sim 300 m_e$) and spin. Short-lived defects are also observed in the near-steady-state PA experiment with relatively low mass ($\sim 5 m_e$), and likely no spin. We suggest that the long-lived defect is a ring-torsional polaron while the short-lived defect is a bond-length order soliton.

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FIGURE CAPTIONS

Fig. 1: Chemical structure of (a) undimerized and (b) bond length and ring torsion angle dimerized PNB.

Fig. 2: Near-steady-state photoinduced absorption spectra of PNB cast on quartz substrate.

Fig. 3: Photoinduced absorption spectra of PNB as powder mixed with KBr. Left scale: Near-steady-state (22.4 Hz light modulation) at 10 K. Right scale: Long-lived (reduced by a factor ~ 400) at 80 K.

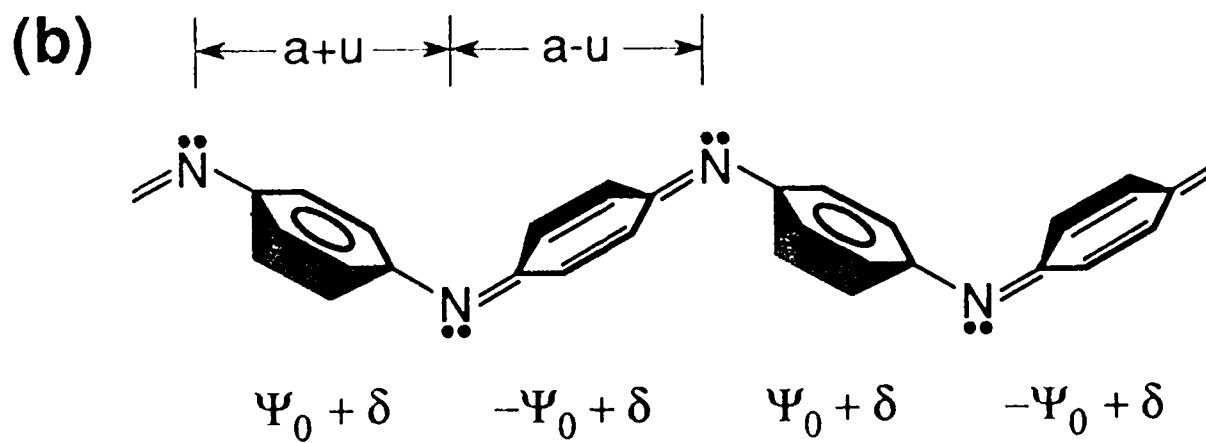
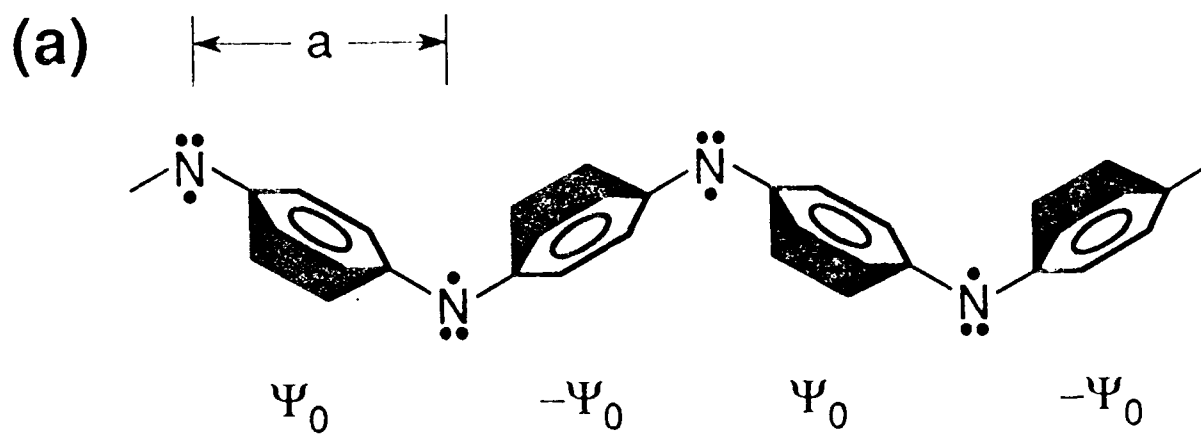


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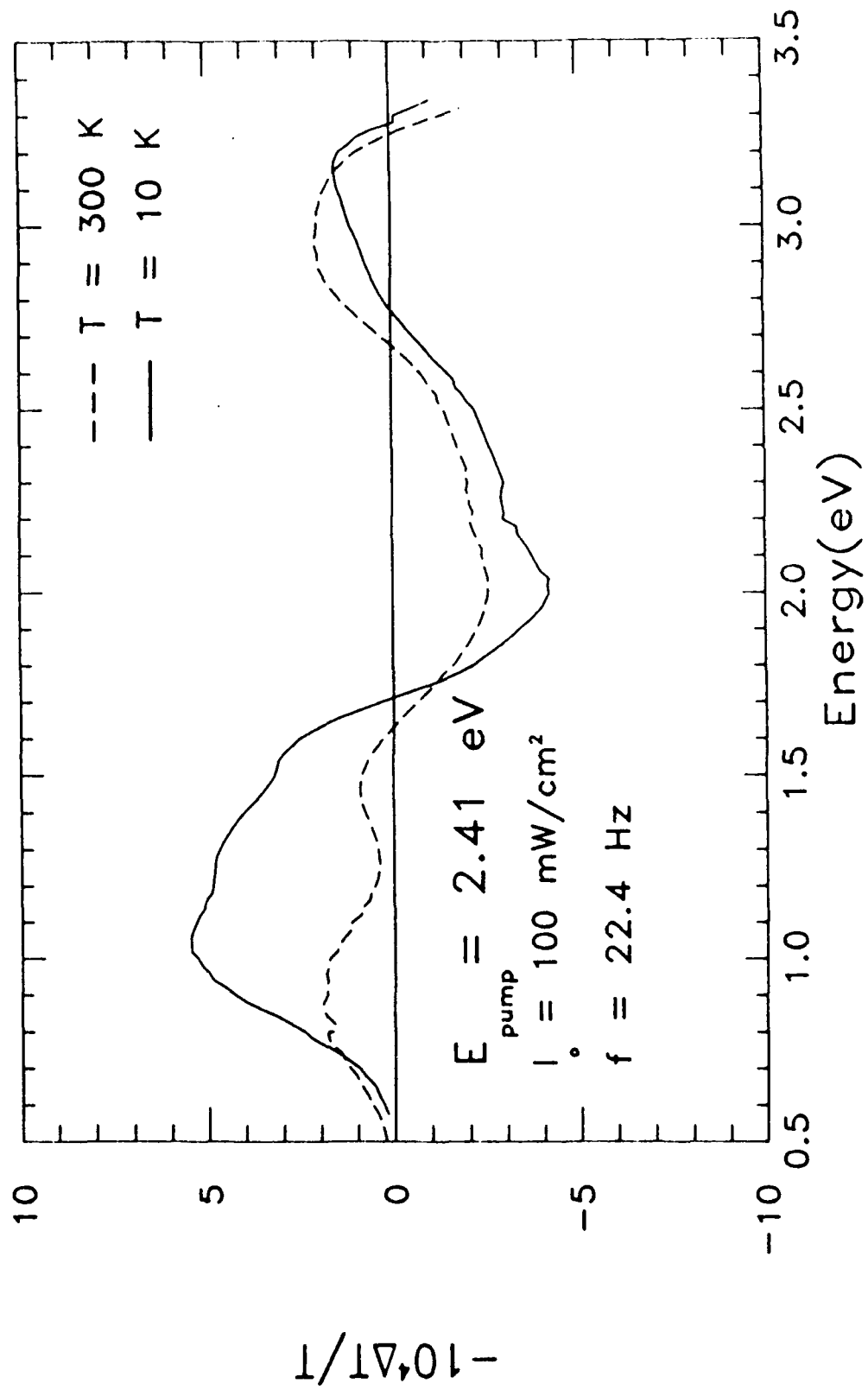


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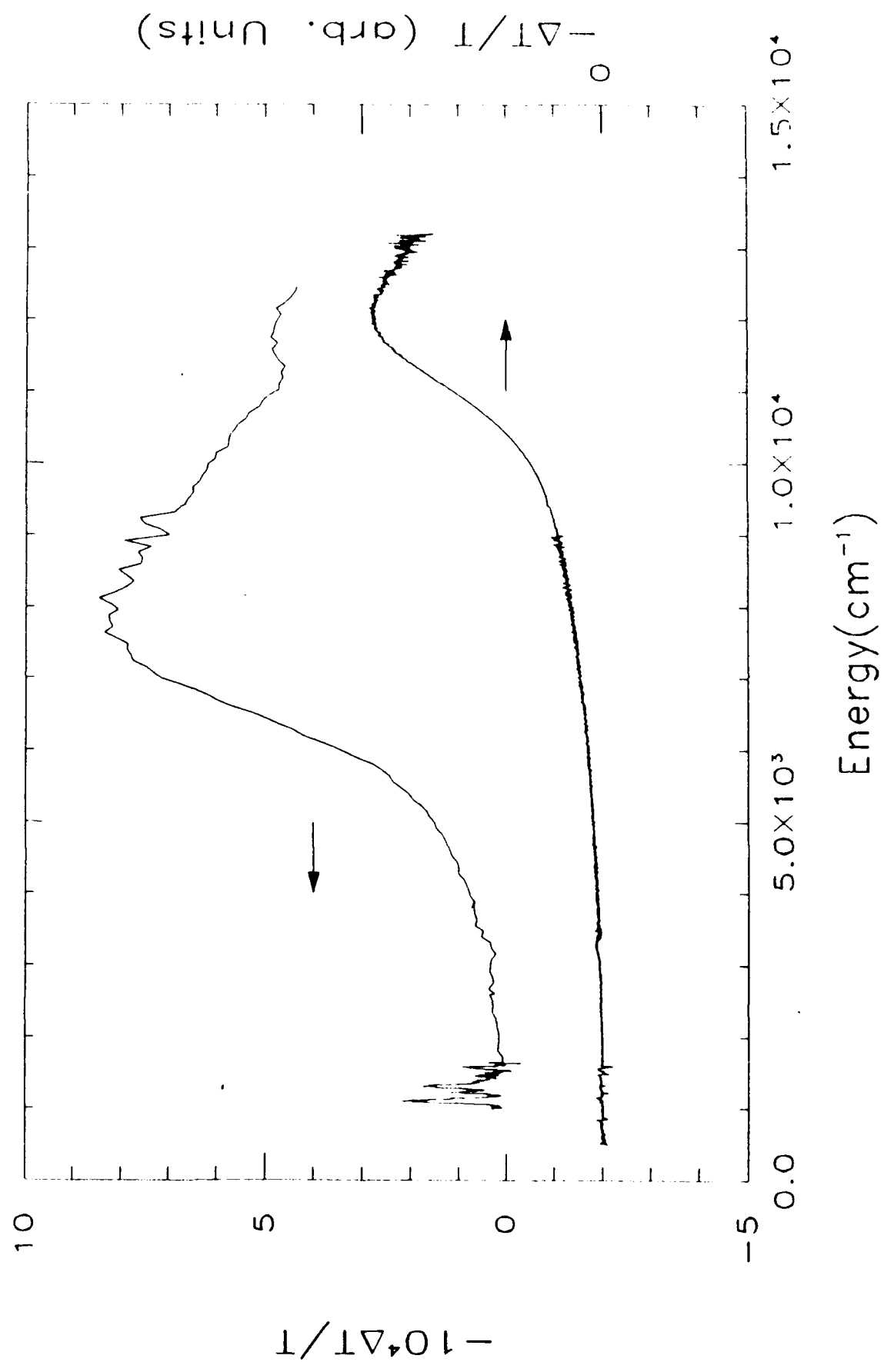


Fig. 3, J. M. Leng et al.